THE APPLICATION OF FT-IR METHODS TO THE CHARACTERIZATION OF COAL LIQUEFACTION PROCESS STREAMS

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INTRODUCTION

Fourier transform infrared spectroscopy (FT-IR) is one of the most versatile analytical techniques available for the study of fossil fuel structure and reaction chemistry [1-5]. Among its advantages are: 1) its ability to study feedstocks and reaction products as solids, liquids and gases, since almost all have characteristic absorptions in the infrared; 2) its high sensitivity, allowing the study of strongly absorbing materials such as coal and char, and the use of techniques such as attenuated total reflectance (ATR) or photoacoustic spectroscopy; 3) its speed, allowing the possibility of following chemical reactions on-line. Because of these advantages, FT-IR spectroscopy has achieved increasing use in fuel science.

The objective of this work was to evaluate the use of two FT-IR methods for characterization of distillation resids from coal liquefaction process streams. The first method is quantitative FT-IR analysis of samples pressed into KBr pellets to determine functional group concentrations. The second method is Thermogravimetric Analysis with FT-IR analysis of evolved products (TG-FTIR). In addition, the application of on-line FT-IR Fiber Optic (F-O) ATR analysis to coal liquefaction processes is addressed.

EXPERIMENTAL

Characterization of Coal Liquefaction Products

The samples used in this study were supplied by Consolidation Coal Company (CONSOL), PA, along with chemical and structural information obtained with various techniques. These samples included: 1) Three feed coals (Wyodak, Illinois, and Pittsburgh); 2) Nine whole resid samples produced by distillation of process oils generated from the three different feed coals and obtained from three different sampling points (interstage, recycle, second stage) during liquefaction runs at the Wilsonville (AL) facility; 3) Nine THF soluble portions of the above whole resids; 4) Four additional solids free resids obtained during a catalyst aging study at the HRI (NJ) facility; 5) A single whole process oil for Pittsburgh coal obtained from the Wilsonville facility. These samples were analyzed by both FT-IR and TG-FTIR.

FT-IR Analysis - The samples are analyzed as KBr pellets in a Nicolet 7199 FT-IR. For quantitative analysis of such spectra, a curve analysis program is employed to synthesize the IR spectra [1-3]. The program uses a basic set of adsorption peaks identified with various functional groups. The synthesis routine can produce a spectrum which matches the actual spectrum well. The correction of a whole resid spectrum for scattering and minerals is demonstrated in Figure 1.

TG-FTIR Analysis - The apparatus consists of a sample suspended from a balance in a gas stream within a furnace. As the sample is heated in helium, the evolving volatile products are carried out of the furnace directly into a gas cell for analysis by FT-IR [5]. The results of a typical resid pyrolysis experiment are shown in Figure 2. The system continuously monitors the time-dependent evolution of the gases and tars, and weight of the non-volatile material. At the end of the pyrolysis experiment, oxygen is introduced to burn the residue to obtain the ash content of the sample.

In-Situ FT-IR/F-O/ATR Measurements

A coal liquefaction test cell which incorporates a FT-IR/F-O system is shown in Figure 3. The reactor is made of 3/8" stainless tubing and Swagelok tube fittings. This reactor can withstand a pressure as high as 3800 psig at 400 °C. A sapphire fiber, which is 15" (38 cm) in length and 0.25 mm in diameter, is used as an ATR sensor in the reactor. A zirconium fluoride fiber cable is used as a transmitting fiber to link between the sensor fiber and the FT-IR spectrometer and detector.

Liquefaction of demineralized Zap lignite was performed in the test cell, with 1 g of coal sample mixed with 6 ml of tetralin. The experiment was performed by heating the reactor from room temperature to 400 °C at 20 °C/min, and sustaining the final temperature for 40 minutes. The F-O/ATR spectra of the tetralin/coal liquid mixtures in the reactor were taken at regular intervals. Tetralin spectra at the relevant temperatures were taken and compared with those from coal liquefaction experiments.

RESULTS AND DISCUSSION

Characterization of Coal Liquefaction Products

Characterization of the samples using the FT-IR and TG-FTIR methods provides a good understanding of the average chemical structure of products from the various stages of a coal liquefaction process. In order to demonstrate the reliability of these two FT-IR techniques, correlation and comparison of the results in this study with those supplied by CONSOL using different methods are described below.

FT-IR Analysis

Aromatic and Aliphatic Hydrogen (Proton) Distribution - The comparison of the aromatic to total hydrogen ratio (H_{ar}/H_{total}) using FT-IR analysis with the aromatic proton fraction from the ^{1}H-NMR method for the THF soluble samples is shown in Figure 4a. Figure 4b shows the comparison of the aliphatic hydrogens for the same set of samples. The results show that the FT-IR H_{ar}/H_{total} agrees reasonably well with the fraction of aromatic protons derived from the ^{1}H-NMR method. The same is true of the aliphatic hydrogen. These figures contain two lines. The solid line is the mean value of the ratios between the two sets of measurements. The dashed line is a parity line. Figures 4a and 4b provide a relation between the results obtained by these two methods:

H_{ar}/H_{total} (%, THF sol.), FT-IR = 0.77 [Aromatic Proton Fraction (% THF sol.), ^{1}H-NMR]
H_{al}/H_{total} (%, THF sol.), FT-IR = 1.1 [Aliphatic Proton Fraction (% THF sol.), ^{1}H-NMR]

Hydroxyl Groups - Both this study and CONSOL used an FT-IR method to determine the

concentration of hydroxyl groups in the samples. CONSOL used the -OH stretch band found between 3200 and 3400 cm^{-1} to determine the phenolic -OH concentration from measurements on THF-soluble portions of the samples. In this study, the concentration of hydroxyl groups was determined using the 3200 cm^{-1} O-H stretch to avoid the interference from the KBr-H$_2$O band which peaks at 3400 cm^{-1} [1]. The hydroxyl results obtained in this study and by CONSOL are in good agreement, considering the differences in sample preparation and the quantitative analysis routines. The relation between them is:

-OH (wt%, THF sol.), FT-IR = 0.90 [Phenolic-OH (wt%, THF sol.), FT-IR | CONSOL]

Oxygen Analysis - In general, most of the oxygen atoms in coal and coal products are contained in hydroxyl, ether, and carbonyl functional groups. In this study, oxygen contents of the samples were determined through quantitative analysis of hydroxyl and ether by the FT-IR method, assuming that the amount of oxygen in carbonyl functions is negligible. The oxygen contents of the samples provided by CONSOL were determined by difference in elemental analyses. The oxygen data in this study and from CONSOL for the whole resids and whole process oil show reasonable agreement, although the data are somewhat scattered. The relation between these two different methods is:

O-Content (wt%, MAF), FT-IR = 1.1 [O-Content (wt%, MAF), Elemental Difference]

Hydrogen Analysis - The total hydrogen content for each of the samples was determined by summing up the aliphatic, aromatic, and hydroxyl hydrogen determined by FT-IR. The hydrogen analysis provided by CONSOL was determined with a Leco CHN-600 elemental analysis instrument. The results of these two methods are in good agreement. The relation between them is:

H-Content (wt%, MAF), FT-IR = 1.1 [H-Content (wt%, MAF), Elemental Analysis]

Carbon Analysis - The carbon content of each sample was determined by mass balance difference with oxygen and hydrogen contents obtained with the FT-IR method, assuming that the fraction of others, such as nitrogen and sulfur, is negligible. The values supplied by CONSOL were obtained from carbon analysis with the Leco CHN-600 instrument. A comparison shows that these two sets of data from different methods are in good agreement, and the relation between them is:

C-Content (wt%, MAF), FT-IR = 1.0 [C-Content (wt%, MAF), Elemental Analysis]

Ash - FT-IR analysis can determine the contents of major minerals, i.e. mixed clays, Kaolinite, Quartz, and Calcite. The total ash content determined by FT-IR is the sum of these four minerals. Since the FT-IR measurement of minerals includes the associated water and is done at ambient temperature, it is expected to be higher than the high temperature ash determinations supplied by CONSOL. However, it is also true that the FT-IR method does not determine pyrite, so it may underestimate the ash content for coals which contain large amounts of this mineral. The comparison of the ash contents determined with FT-IR and by CONSOL is shown in Figure 4c. The results show that the trends in the FT-IR values of the total ash content agreed well with the values supplied by CONSOL, although the latter numbers were lower as expected. The relation between the two measurements is:

Ash (wt%, dry),FT-IR = 1.3 [Ash (wt%, dry), Combustion]

TG-FTIR Analysis

Proximate Analysis of Feed Coals - Pyrolysis up to 900 °C followed by combustion of the residue, when carried out in the TG-FTIR apparatus, gives a good proximate analysis for feed coals. The proximate analysis with TG-FTIR reveals the contents of ash, volatile matter, fixed carbon, and moisture in coal.

Pyrolysis of coal at temperatures as high as 900 °C will produce a char with a high carbon content (>95%, MAF). Therefore, the char yield (MAF) in pyrolysis represents the fixed carbon content in the coal. The comparison of the fixed carbon content obtained by TG-FTIR and that supplied by CONSOL is shown in Figure 4d. It shows that the two sets of values are in good agreement and the relation between them is:

Fixed Carbon (wt%, dry), TG-FTIR = 1.0 [Fixed Carbon (wt%, dry), Proximate Analysis]

The ash content is determined by burning the char in the presence of oxygen. A comparison of ash analyses is shown in Figure 4e, and the results show a good agreement. The relation between the two sets of data is:

Ash (wt%, dry), TG-FTIR = 1.1 [Ash (wt%, dry), Proximate Analysis]

The volatile matter of coal includes all the species evolved during pyrolysis. These species are gases and tars, which are measured by TG-FTIR during the process of pyrolysis. The comparison of the volatile matter contents determined by TG-FTIR with those provided by CONSOL from proximate analysis is shown in Figure 4f. The results show that they are in good agreement with each other and the relation is:

Volatile (wt%, dry), TG-FTIR = 1.0 [Volatile (wt%, dry), Proximate Analysis]

The moisture content of coal is determined by TG-FTIR prior to pyrolysis. The results obtained by TG-FTIR are not in good agreement with those supplied by CONSOL, although the trend is correct. The relation between them is:

Moisture (wt%, as rec.), TG-FTIR = 0.45 [Moisture (wt%, as det.), Proximate Analysis]

This difference is not surprising since the moisture content depends on how the sample is stored and handled.

Ash Analysis for Resids - The ash content of the distillation resids was determined using TG-FTIR by burning the char residue from the resids in the presence of oxygen. The comparison of the resid ash content obtained with TG-FTIR and that supplied by CONSOL is shown in Figure 5a. The results show that the ash contents determined by TG-FTIR are in very good agreement with those provided by CONSOL. The relation between the two sets of data is:

Ash (wt% dry), TG-FTIR = 1.0 [Ash (wt%, dry), Combustion]

Char Analysis for Resids - Coal chars produced at temperatures above 900 °C consist mainly of large condensed aromatic rings. It is expected that the char yield from resid pyrolysis would have a proportional relation with the content of condensed aromatics. The comparison of the char yield for pyrolysis performed in the TG-FTIR and the condensed aromatic proton fraction from NMR is shown in Figure 5b for the THF soluble fractions. The results show that the char

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yield in resid pyrolysis increases with increasing condensed aromatic proton fraction. The relation between the two sets of values is:

Char (wt%,THF sol.), TG-FTIR = 0.65 [Cond. Aromatic Proton (%, THF sol.) ^{1}H-NMR]

Data Interpretation in the Context of the Liquefaction Process

The samples from the Wilsonville facility were taken from three locations to represent different degrees of coal processing. The Interstage Product samples were distillation resids obtained from a high pressure flash separation system located between the first stage and second stage reactors. The 2nd Stage Product samples were resids collected from the bottom product hold tank of a separation system following the second stage reactor. The Recycle samples were resids obtained from the solvent surge tank. The Recycle samples are the partially deashed products of the 2nd Stage Product. The structural differences of the samples, revealed in the analytical data, are due to differences in the feed coals and to different degrees of coal processing in liquefaction, as discussed below.

A comparison of -OH contents from THF soluble fractions of the resid samples from different degrees of processing is shown in Figure 6. The results show that the Interstage Product has a higher -OH content than the 2nd Stage Product due to upgrading by the second reactor. The TG-FTIR results show a corresponding reduction of CO evolution in pyrolysis for the 2nd Stage Product, as discussed below. Figure 6 shows a slight -OH reduction due to the deash process. In general, the -OH content of the resids decreases in the order Interstage > 2nd Stage > Recycle. The trends for char yield from TG-FTIR analysis follow the same general order, which is consistent with the role of oxygen functions in retrogressive reactions under pyrolysis [6] and liquefaction conditions [7].

Since the oxygen content of the feedstock would be reduced in the liquefaction process, the amount of CO evolution in pyrolysis is expected to decrease in the order coal > Interstage > 2nd Stage > Recycle, and the results shown in Figure 7 for the whole resids indicate that this is the case. If the results in Figures 6 and 7 are compared, it can be seen that the -OH content and the CO evolution from pyrolysis are related.

Similar to the result of CO evolution in pyrolysis, more CH_4 is evolved in coal pyrolysis than in resid pyrolysis. Because most of the CH_4 forming components in coal are consumed in the liquefaction process in which gaseous product CH_4 is separated from the process stream to become fuel gas, it is reasonable to see less CH_4 evolution in resid pyrolysis. A comparison of CH_4 yields from pyrolysis of the feed coals and various whole resid samples is shown in Figure 8. Since CH_4 forming components would be further reduced by the Second stage reactor, it is also not surprising to see less CH_4 evolution in the pyrolysis of the 2nd Stage Product than the Interstage Product. The amounts of CH_4 evolution from the 2nd Stage Product and from the Recycle are similar, which reveals that the deash process has little effect on the CH_4 forming structures in resids. In general, the amount of CH_4 evolution in the pyrolysis of liquefaction products follows the order coal > Interstage > 2nd Stage ~ Recycle.

The hydrogen content analyses indicate a slight increase in hydrogen concentration in the whole resids from the second stage reactor by comparing the 2nd Stage Product with the Interstage Product (except for Pittsburgh resid). These results are shown in Figure 9. This figure also shows the expected increase in hydrogen concentration for the resid products when compared to the feed coal. Also, as the material is upgraded, the absolute amount of aromatic hydrogen decreases, as shown in Figure 10.

The HRI samples represent production of material from a Continuous Two-Stage Liquefaction facility for different periods of time in a single run. Interpretation of the data reveals a consistent variation of the properties of the samples with the length of run period. The interpretation of these variations is discussed below and is based on information supplied by CONSOL on variations in run conditions as function of time.

The variation of the hydrogen content of the sample with the length of the run period is shown in Figure 11. The results show that the total hydrogen and aliphatic hydrogen content decrease with increasing run time, whereas the aromatic hydrogen shows an opposite trend. The decrease of the hydrogen content of the liquefaction product with run time may be attributable to catalyst aging as well as to a reduction in the solvent/coal ratio and an increase in solvent cut point. It is reasonable to observe a reduction in the aliphatic hydrogen content since the hydrogenation rate slows down with time due to catalyst aging. The increase in H_{ar} with run time may also result from the increasing reaction temperature which would tend to increase the amount of aromatic hydrogen.

The variation of the hydroxyl and ether contents of the samples with the length of the run period is shown in Figure 12. The results show an increase of the hydroxyl content with run time. The change in -OH concentration is due to catalyst aging as well as to the reduction in the solvent/coal ratio and to the increase in solvent cut point. The FT-IR results also show an increase in the ether content with time. The increase of the ether content in the liquefaction products can be attributed mostly to the catalyst aging which would result in a lower rate of bond cleavage on ether linkages. A second possibility is an increase in the amount of ethers formed from retrogressive reactions involving hydroxy and dihydroxy functionalities structures.

In-Situ FT-IR/F-O/ATR Measurements

In order to accommodate the temperature (~400 °C) and pressure (~3000 psig) requirements of a coal liquefaction process, a sapphire fiber optic element was used in the ATR mode for in-situ measurements. This cuts out the information below about 2500 cm^{-1}, but still allows significant amounts of chemical structural information to be obtained.

Since tetralin is the solvent used in coal liquefaction experiments, it is of interest to know how tetralin behaved under temperature conditions similar to those of coal liquefaction. Non-isothermal experiments which simulate the conditions of coal liquefaction are carried out in the test cell, and the infrared spectra from the F-O/ATR spectroscopy at different temperatures were obtained. Figure 13 shows the tetralin absorbance spectra in the C-H stretching region at different temperatures. Since tetralin does not contain oxygen functional groups, the focus of the analysis was on the C-H stretching region.

It can be seen from the spectra that the infrared absorbance decreases with temperature. This result is expected, since the depth of penetration of the infrared evanescent wave into the sample decreases with temperature. The temperature effect on F-O/ATR spectroscopy requires further study in order to obtain quantitative results.

Since it was known [8] that tetralin would undergo hydrogen transfer reactions to form a mixture of aliphatic and alkyl aromatic compounds by heat treatment, the aliphatic to aromatic ratio in the system would therefore vary with temperature. Based on Figure 13, one should be able to determine the aliphatic to aromatic hydrogen ratios at different temperatures from the absorbance ratios of 2930 cm^{-1} to 3020 cm^{-1}, if the extinction coefficients for each species were

known. This issue, for pure tetralin as well as coal liquefaction measurements, will be discussed in a future publication.

It has been reported [9] that the alkyl CH_3 gives rise to a symmetric stretching mode at 2870 cm^{-1}, and the -CH_2- at 2850 cm^{-1}. Since tetralin does not contain methyl structures, the 2860 and 2840 cm^{-1} peaks shown in Figure 13 are actually from the spliting of the methylene symmetric stretching at 2850 cm^{-1}. By thermal treatment, tetralin will undergo decomposition to form its derivatives, which contain methyl groups. The methyl symmetric stretching at 2870 cm^{-1} would interfere with the 2860 cm^{-1} peak from the methylene, and, therefore, the former peak would not be distinct if its concentration is low. Because of this interference, we cannot see a 2870 cm^{-1} peak emerging at higher temperatures in Figure 13. However, if a series of absorbance spectra from coal liquefaction experiments are examined, as shown in Figure 14 for demineralized Zap, the emergence of the methyl 2870 cm^{-1} absorbance underneath the methylene 2860 cm^{-1} absorbance can be clearly seen. A curve resolving technique has recently been developed in our group to resolve overlapped absorption bands. This technique will be applied to the F-O/ATR spectra to improve quantitative analysis.

The O-H stretching region for the liquefaction run is shown in Figure 15. The absorbance spectrum of O-H stretching is usually a broad band, ranging between 3100 and 3600 cm^{-1} and centered near 3400 cm^{-1} [10]. Figure 15 shows that the absorbance by hydroxyls increases with the degree of liquefaction, indicating increasing amount of OH-containing coal fragments dissolved in the liquid phase.

CONCLUSIONS

Both FT-IR and TG-FTIR have been clearly shown to provide a wide variety of useful information for process stream characterization. Both techniques can be applied to whole process oils, resids, or distillates, including ash components, and require relatively small samples (<50 mg). Significant differences are observed between process stages, coal types, and with catalyst aging. A summary of the composition parameters that can be obtained by FT-IR and TG-FTIR is shown in Table 1. In many respects, FT-IR is probably the single most useful technique for this purpose, since it can provide measurements on both organic and mineral components. It has also demonstrated that on-line FT-IR measurements could be made in-situ using a sapphire fiber optic element in the Attenuated Total Reflectance mode.

ACKNOWLEDGEMENTS

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TABLE 1. SUMMARY OF FT-IR AND TG-FTIR MEASUREMENTS

FT-IR MEASUREMENT	ALTERNATIVE TECHNIQUE
Hydroxyl Hydrogen	Chemical Titration
Aliphatic Hydrogen	^{1}H-NMR
Aliphatic Carbon*	^{13}C-NMR
Aromatic Hydrogen	^{1}H-NMR
Hydrogen Content	Elemental Analysis
Carbon Content*	Elemental Analysis
Hydroxyl Oxygen	Chemical Titration
Ether Oxygen	- - -
Carbonyl Oxygen**	- - -
Total Ash	TGA
Mineral Components	ICP

| TG-FTIR MEASUREMENT	ALTERNATIVE TECHNIQUE
Direct	
Volatile Content	Proximate Analysis
Fixed Carbon	Proximate Analysis
Total Ash	Proximate Analysis
Moisture	Proximate Analysis
C,H,N,S	Elemental Analysis
Indirect	
Char Yield →Condensed Aromatics	^{1}H-NMR
CO Yield → Phenolic Content	FT-IR
CH₄ Yield → Methyl Group Content	^{13}C-NMR
Tar Evolution Profile → Boiling Range	Distillation
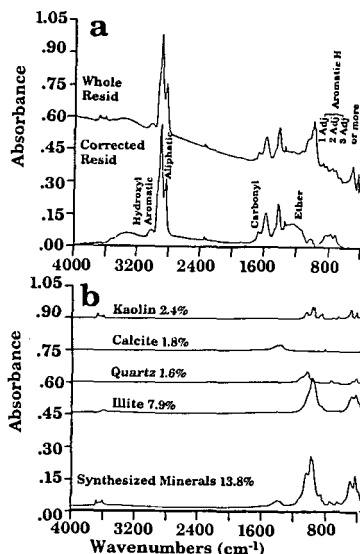
Figure 1. Quantitative FT-IR Analysis of the Coal Liquefaction Product. Correction of Resid Spectrum for Scattering and Minerals. a) Correction of Resid Spectrum; b) Determination of Mineral Spectrum by Addition of Reference Spectra. Data for Whole Resid Sample (interstage) from Illinois No. 6 Coal.
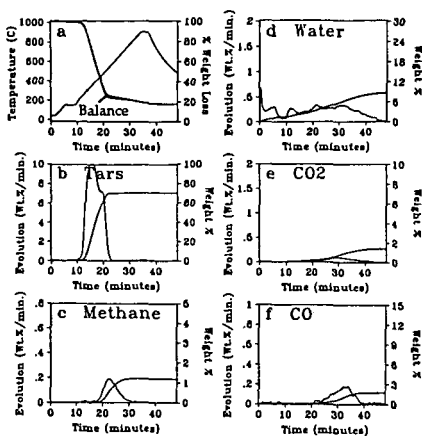
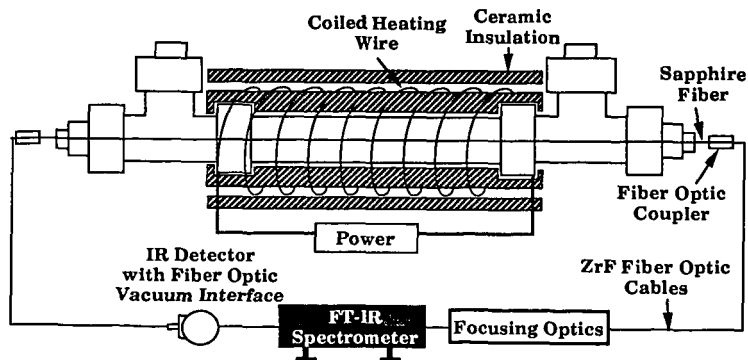**Figure 2.** TG-FTIR Results for Interstage Oil Resid from Illinois No. 6 Coal.

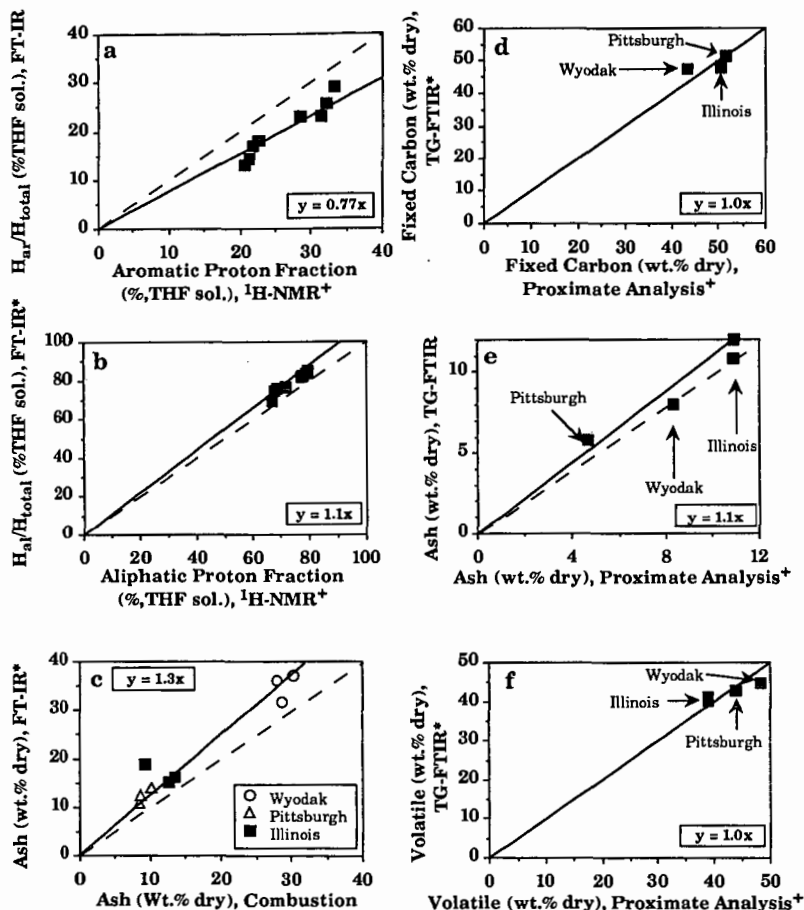**Figure 3.** Schematic of FT-IR Fiber-Optic ATR System for Coal Liquefaction.

Figure 4. Correlation and Comparison of the Results from FT-IR Techniques and Other Methods. a) Resid Aromatic Hydrogen Distribution; b) Resid Aliphatic Hydrogen Distribution Resid; c) Resid Ash Content; d) Coal Fixed Carbon; e) Coal Ash Content; f) Coal Volatile. * Present Study; + Data Supplied by CONSOL.
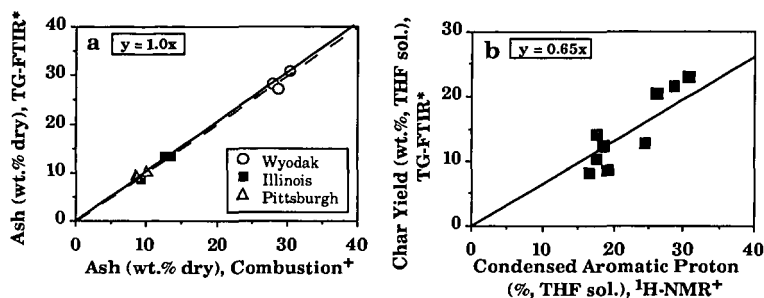
Figure 5. Correlation and Comparison of the Results from FT-IR Techniques and Other Methods. a) Resid Ash Content; b) Char Yield with Condensed Aromatic Proton Fraction. * Present Study; + Data Supplied by CONSOL.
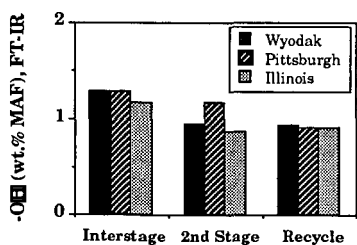
Figure 6. -OH Content at Different Stages for Wilsonville Resids.
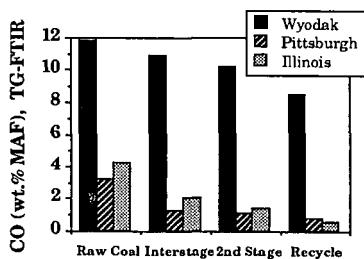
Figure 7. CO Evolution from Pyrolysis of Wilsonville Resids.
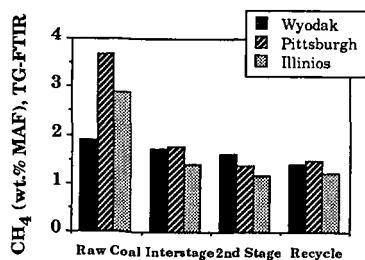
Figure 8. CH_4 Evolution from Pyrolysis of Wilsonville Resids.
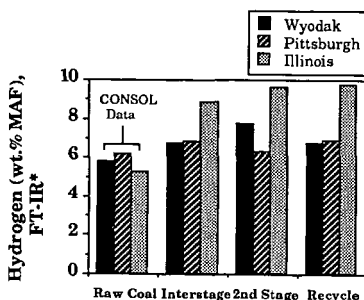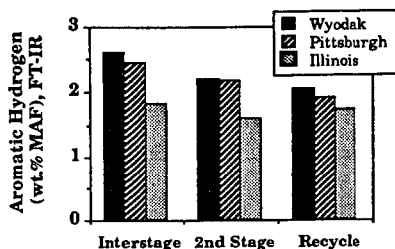

Figure 9. Hydrogen Content at Different Stages for Wilsonville Resids.

Figure 10. Aromatic Hydrogen Content at Different Stages for Wilsonville Resids.
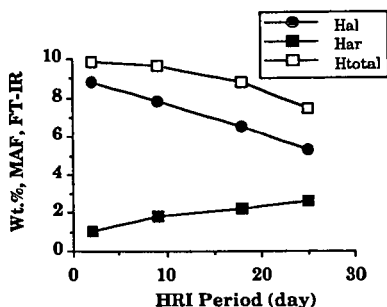
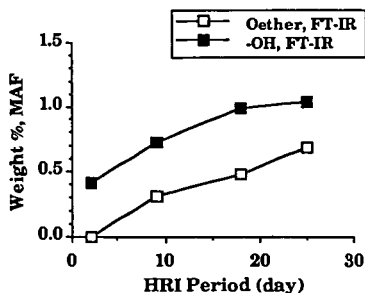**Figure 11.** Hydrogen Analysis for HRI Liquids.

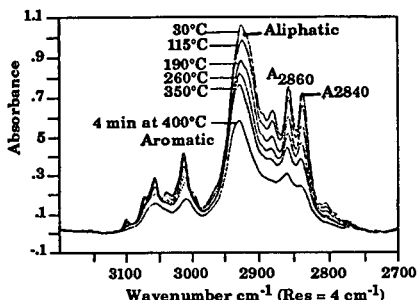**Figure 12.** Oxygen Functional Group Analysis for HRI Liquids.

Figure 13. The Absorbance Spectra of Tetralin from F-O/ATR Spectroscopy in a Non-Isothermal Experiment.
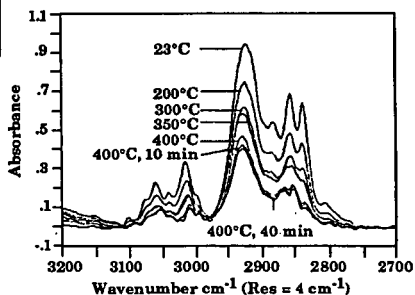

Figure 14. The C-H Stretching Region of the Absorbance Spectra from F-O/ATR Measurements under Coal Liquefaction Conditions for Demineralized Zap.
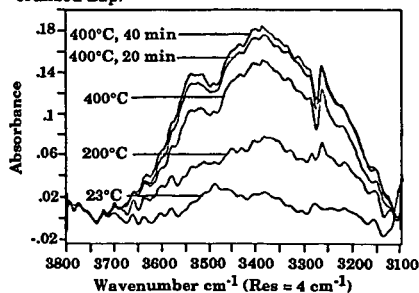

Figure 15. The O-H Stretching Region of the Absorbance Spectra from F-O/ATR Measurements under Coal Liquefaction Conditions for Demineralized Zap.